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Optical absorption spectra and energy gap studies of Pr^{3+} doped chloroborate glasses

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Abstract : The optical properties of Pr^{3+} doped chloroborate glasses are studied. The values of energy band gaps are reported for four Pr^{3+} doped chloroborate glasses Using Judd-Ofelt theory, radiative transition probabilities (A), radiative lifetimes (τ_R), branching ratios (β) and integrated absorption cross sections (Σ) are estimated theoretically for certain excited states of Pr^{3+} doped different chloroborate glasses.

Keywords : Optical absorption, optical band gap, radiative lifetime

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There is an increase of interest on the optical properties of glassy and amorphous semiconductors doped with small amounts of rare earth ions. These glasses are potential materials for laser action. Previously, we have reported the spectroscopic investigations of Pr^{3+} doped in different sulphate glasses [1] and in different fluoroborate glasses [2]. The present investigation aims at studying the optical properties of Pr^{3+} doped different chloroborate glasses. Samples of different chloroborate glasses in the composition range $80H_3BO_3$–$10Na_2CO_3$–10RCl (R = Li, Na, K and Cd) doped with Pr^{3+} have been prepared. Spectroscopic properties and the optical band gaps of these samples are reported in order to investigate their possible technological applications.

Glasses with batch compositions $80H_3BO_3$–$10Na_2CO_3$–10RCl (R = Li, Na, K and Cd) were prepared using quenching technique. These glasses were obtained by melting appropriate amounts of H_3BO_3, Na_2CO_3, different chlorides and Pr_2O_3 (0.2 mol%) in a special mud crucible for 2 hours at temperatures between 900°C and 1100°C depending on the composition and quenching between two ceramic tiles. Undoped glasses were prepared

for use in reference samples. Optical spectra were taken from 200 nm to 800 nm in Hitachi 150–20 double beam spectrophotometer. Densities of the samples were measured using xylene as immersion liquid with an accuracy of ± 0.005 and the refractive indices were measured using an Abbe refractometer.

Optical absorption :

In crystalline materials, the optical band gap is directly obtained from the absorption. However for amorphous materials, the optical gap is estimated from the optical absorption at the fundamental edge using the theory of Davis and Mott [3]. The absorption in amorphous semiconductors obeys a quadratic relation for the inter-band non-direct transitions. Hence a plot of $[\hbar\omega\alpha(\omega)]^{1/2}$ and $[\hbar\omega]$ is a straight line for all the samples studied. Optical absorption spectra of Pr^{3+} doped different chloroborate glasses and the plot of $[\hbar\omega\alpha(\omega)]^{1/2}$ *vs* $[\hbar\omega]$ are shown in Figures 1 and 2 respectively.

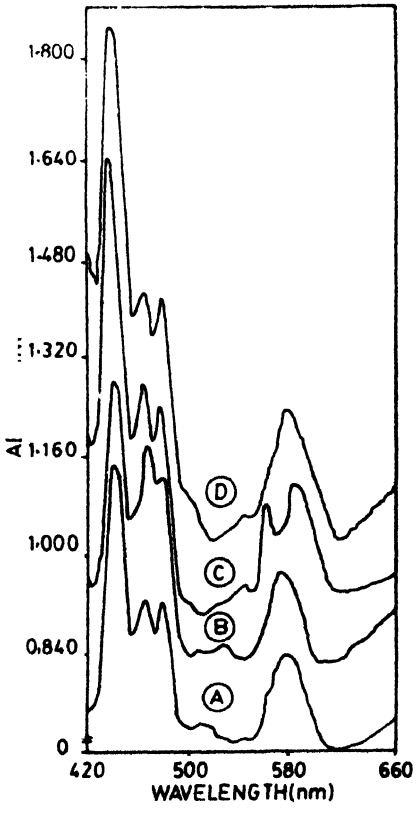

Figure 1. Absorption spectra of Pr^{3+} doped chloroborate glasses. (A) Lithium chloroborate glass, (B) sodium chloroborate glass, (D) potassium chloroborate glass and (C) cadmium chloroborate glass.

From Figure 1, it is observed that the position of the fundamental absorption edge shifts to longer wavelengths with an increase of atomic weight of the alkali elements.

Among these four glasses, cadmium chloroborate glass shows the largest shift of the absorption edge. Optical band gaps for different Pr^{3+} doped chloroborate glasses were

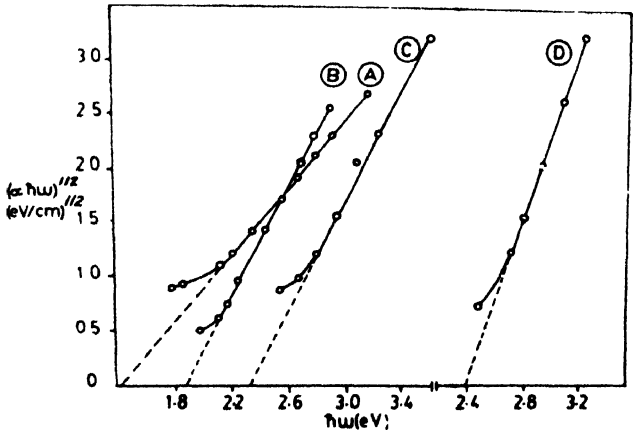

Figure 2. $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy $\hbar\omega$ for different chloroborate glasses (A) Lithium chloroborte glass, (B) sodium chloroborate glass, (D) potassium chloroborate glass and (C) cadmium chloroborate glass.

obtained by extrapolating the linear part of the curve to $(\alpha\hbar\omega)^{1/2} = 0$ as shown in Figure 2. These values are given below.

Glass	Thickness (mm)	Refractive index	Optical band gap (eV)
Lithium chloroborate glass	1.425	1.496	1.44
Sodium chloroborate glass	1.600	1.512	1.88
Potassium chloroborate glass	2.676	1.501	2.34
Cadmium chloroborate glass	3.202	1.492	2.40

From the above data it is observed that the optical band gaps increase with increase of the atomic weight of the alkali elements. Similar results have been observed in the case of Er^{3+} doped chloroborate glasses [4].

Electronic energy levels and intensity parameters :

The absorption spectra of Pr^{3+} doped different chloroborate glasses are shown in Figure 1. Though the recorded spectra appear similar to each other, the intensities of the corresponding bands change with the environment. The Russel-Saunder term symbols, the barycentres of the corresponding transitions as well as the experimental and theoretical oscillator strengths of different absorption bands in four chloroborate glasses are presented in Table 1.

Applying Judd-Ofelt theory [5,6] to the measured intensities, the intensity parameters $(\Omega_2, \Omega_4, \Omega_6)$ were determined by a least square fit. In the above intensity

Table 1. Experimental energy values (E_{exp}), experimental and calculated oscillator strengths (f_{exp} and f_{cal}) and Judd-Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) of Pr^{3+} in different chloroborate glasses.

S. No	Energy level	LCB glass			SCB glass			PCB glass			CCB glass		
		E_{exp}	f_{exp}	f_{cal}	E_{exp}	f_{exp}	f_{cal}	E_{exp}	f_{exp}	f_{cal}	E_{exp}	f_{exp}	f_{cal}
1	$^1D_2$	17296	4.337	4.443	17236	4.008	4.013	17118	2.329	2.332	17060	1.877	1.879
2	$^3P_0$	20871	3.760	6.050	20827	8.501	10.117	21002	3.154	3.363	20826	2.055	1.943
3	$^3P_1$	21499	8.533	6.135	21361	11.900	10.214	21546	3.619	3.397	21453	1.855	1.970
4	$^3P_2$	22721	14.223	14.224	22618	12.928	10.932	22877	7.554	7.555	22721	6.665	6.665
rms deviation :				± 3.317			± 3.072			± 0.305			± 0.160
	$\Omega_2 \times 10^{20}$		12.885			− 1.915			8.116			− 15.682	
	$\Omega_4 \times 10^{20}$		10.428			17.293			5.740			3.367	
	$\Omega_6 \times 10^{20}$		25.872			21.300			13.528			12.564	

LCB glass : Lithium chloroborate glass PCB glass : Potassium chloroborate glass

SCB glass : Sodium chloroborate glass CCB glass : Cadmium chloroborate glass

parameters calculations, the used squared reduced matrix elements were taken from Carnall *et al* [7] as these values are insensitive to the environment. The quality of the fit is estimated by the root mean square deviation which are presented in Table 1. These values are very low. The calculated Judd-Ofelt intensity parameters ($\Omega_2, \Omega_4, \Omega_6$) are also presented in Table 1. For lithium and potassium chloroborate glasses the intensity parameters are in $\Omega_6 > \Omega_2 > \Omega_4$ order whereas for sodium and cadmium chloroborate glasses the order of intensity parameters is $\Omega_6 > \Omega_4 > \Omega_2$. The negative value of Ω_2 for these two glass systems may be due to the proximity of the $5d$ band of Pr^{3+} to $4f$ band and of strong f–d mixing [8].

Radiative properties :

Once the Judd-Ofelt parameters are known, the radiative transition probabilities for any electric dipole transition can be calculated. The radiative transition probabilities (A) are calculated according to

$$A(\psi J, \psi' J') = \frac{64\pi^4 e^2 \upsilon^3}{3h(2J+1)} \cdot \frac{n(n^2+2)^2}{9} \times S_{ed},$$

where ν is the mean energy of the transition. The total radiative transition probability is the sum of all these transition probabilities. The radiative lifetimes (τ_R) for the excited states $^3P_0$,$^1D_2$ and $^3F_3$ of Pr^{3+} in different chloroborate glasses were theoretically estimated from the above total radiative transition probabilities and are presented in Table 2 along with the lithium and potassium fluoroborate glasses. From the table it is observed that the lifetimes of $^3P_0$ and $^3F_3$ are increasing with the weight of the alkali elements. It is also observed that the lifetime values are very high in the case of lithium and potassium fluoroborate glasses for all the states.

Table 2. Radiative lifetimes (τ_R) (μs) for the excited states $^3P_0$, $^1D_2$ and $^3F_3$ states of Pr^{3+} in different chloroborate glasses and fluoroborate glasses.

S. No	State	LCB glass	SCB glass	PCB glass	CCB glass	LFB glass	PFB glass [2]
1	$^3P_0$	10	12	27	16	195	27
2	$^1D_2$	81	231	138	151	2474	467
3	$^3F_3$	493	548	932	4545	9306	1794

LCB glass : Lithium chloroborate glass
SCB glass : Sodium chloroborate glass
PCB glass : Potassium chloroborate glass
CCB glass : Cadmium chloroborate glass
LFB glass : Lithium fluoroborate glass
PFB glass : Potassium fluoroborate glass

The estimated branching ratios (β) and integrated absorption cross sections (Σ) for $^3P_0$ and lower lying states of Pr^{3+} in different chloroborate glasses along with the lithium and potassium fluoroborate glasses are presented in Table 3. It is also observed that all the transitions, except $^3P_0 \rightarrow {}^3H_4$ transition, are having lower values of branching ratios and integrated absorption cross sections when chlorine atoms are replaced by fluorine atoms.

Table 3. Branching ratios (β) and integrated absorption cross sections (Σ) of $^3P_0$ and different lower lying states of Pr^{3+} in different chloroborate glasses and fluoroborate glasses [2].

Transition	LCB glass		SCB glass		PCB glass		CCB glass		LFB glass		PFB glass	
	β	$\Sigma(10^{-18})$	β	$\Sigma(10^{-18})$	β	$\Sigma(10^{-18})$	β	$\Sigma(10^{-18})$	β	$\Sigma(10^{-18})$	β	$\Sigma(10^{-18})$
$^3P_0 \rightarrow {}^1G_4$	0.021	8.53	0.034	13.38	0.031	4.71	0.007	2.45	0.02	0.06	0.03	5 91
$\rightarrow {}^3F_4$	0.078	21.10	0.140	34.23	0.115	11.67	0.032	6 35	0.11	1.77	0.14	16.47
$\rightarrow {}^3F_2$	0.344	77.73	0.060	11.67	0.057	4.92	0.643	94.34	0.12	1.42	0.01	1 04
$\rightarrow {}^3H_6$	0.190	39.85	0.176	32.62	0.263	20.87	0.137	19.09	0.16	1.88	0.07	6.35
$\rightarrow {}^3H_4$	0.364	48.10	0.709	80.49	0.533	26.78	0.178	15.45	0.59	4.17	0.74	38.55

LCB glass : Lithium chloroborate glass

SCB glass : Sodium chloroborate glass

PCB glass : Potassium chloroborate glass

CCB glass : Cadmium chloroborate glass

LFB glass : Lithium fluoroborate glass

PFB glass : Potassium fluoroborate glass

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